Aerosol Chemical Characterization on Board the DOE G1 Using the PILS-IC Technique During TEXAQS 2000

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Why Determine Aerosol Chemical Composition?

- *Sources and precursors*
- *Formation mechanisms*
- *Chemical evolution*
- *CCN properties*
- *Optical effects*
- *Health effects*

Principle of the PILS Technique

- Aerosol particles are grown to super micron size under supersaturation conditions created by mixing sample air with steam; particles of 100 nm diameter are activated with a >90% efficiency.

- The resulting super micron size liquid droplets are collected by a single orifice jet impactor; $D_p(50)$ is ~1 μm.

Principle of the PILS Technique (continued)

- Liquid sample collected at the impactor surface is transported to the IC's with a constant carrier flow (ca. 0.2 mL min^{-1})
- Samples are injected for analysis every 3 minutes, which is the time required to elute the major ions.
- Sample integration time is governed by the carrier flow rate and the sample loop size and was 120 s during TexAqs 2000.

IC Analysis

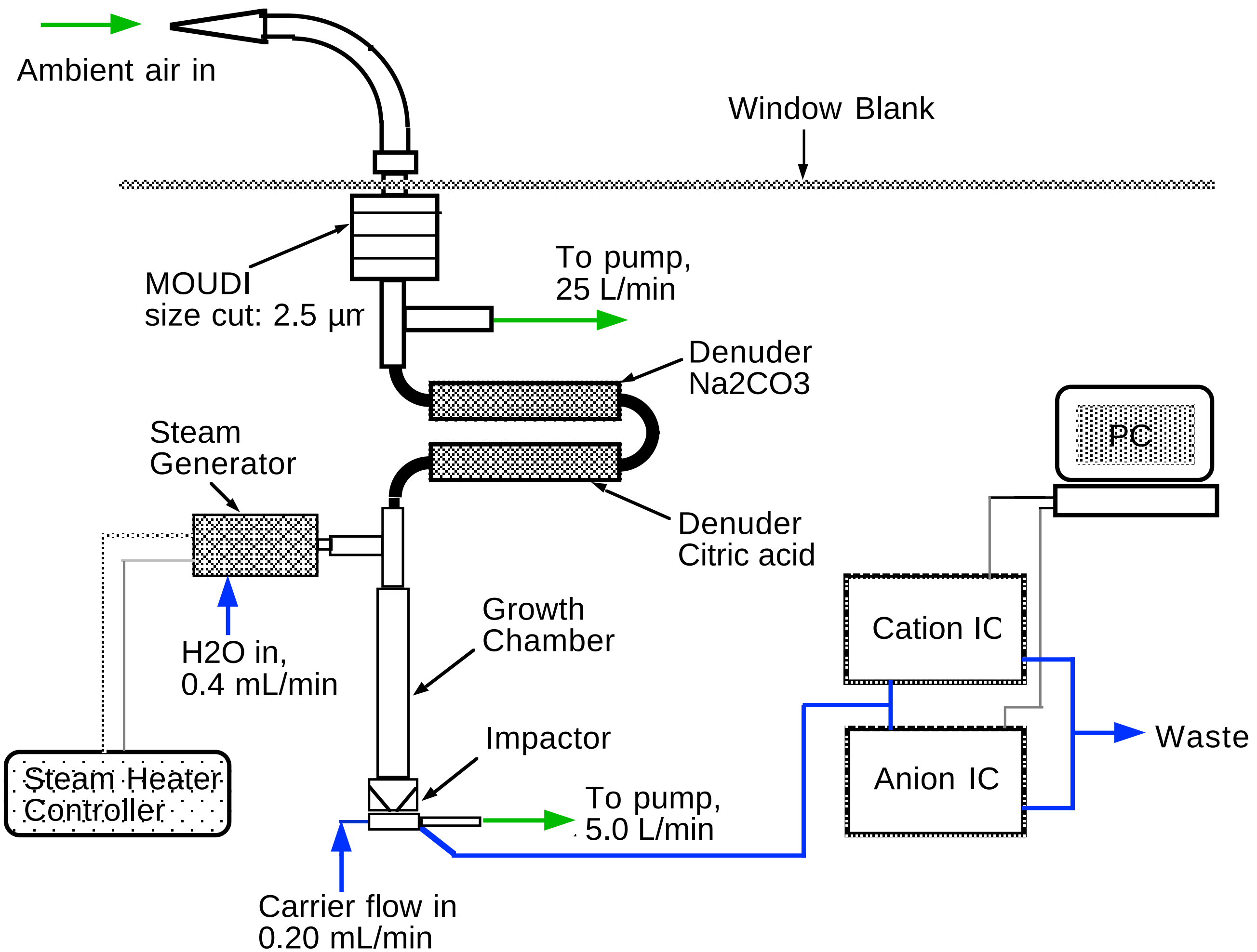
- Cations, Na^+, NH_4^+, K^+, and Ca^{2+}, and anions, Cl^-, NO_3^-, and SO_4^{2-} were determined.

- The limit of detection, based on the IC analysis (ca. 0.1 μM) and a sample air flow rate of 5.0 L min^{-1}, is ~0.1 μg m^{-3} for these ions.

Inlet Arrangement

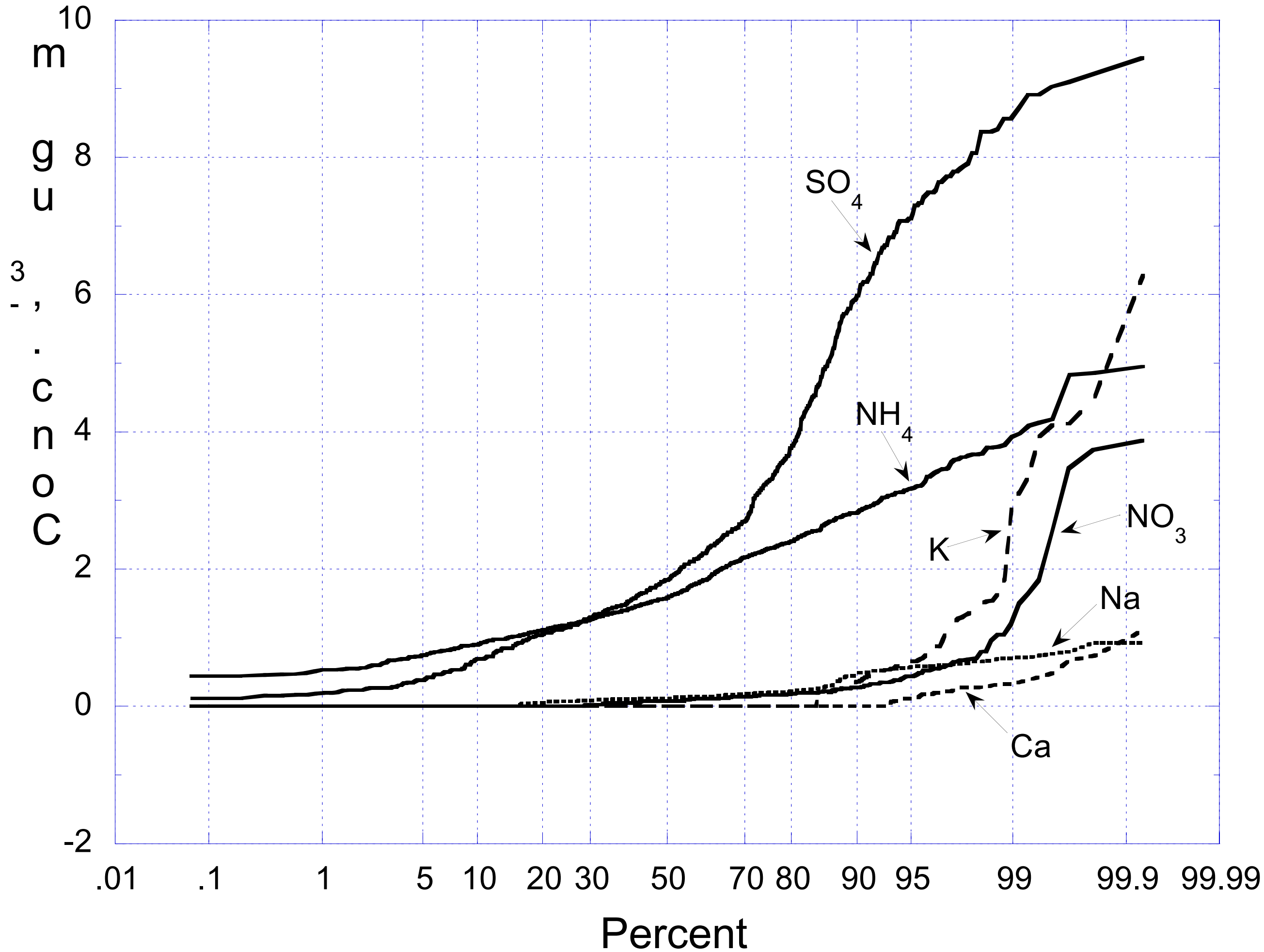
- Isokinetic sampling at a 30 L min^{-1} flow rate.
- A 2.5 μm size cut achieved by a MOUDI impactor.
- SO_2, HNO_3, and NH_3 removed using two glass annular denuders in series.

Schematic Diagram of the G1 PILS System

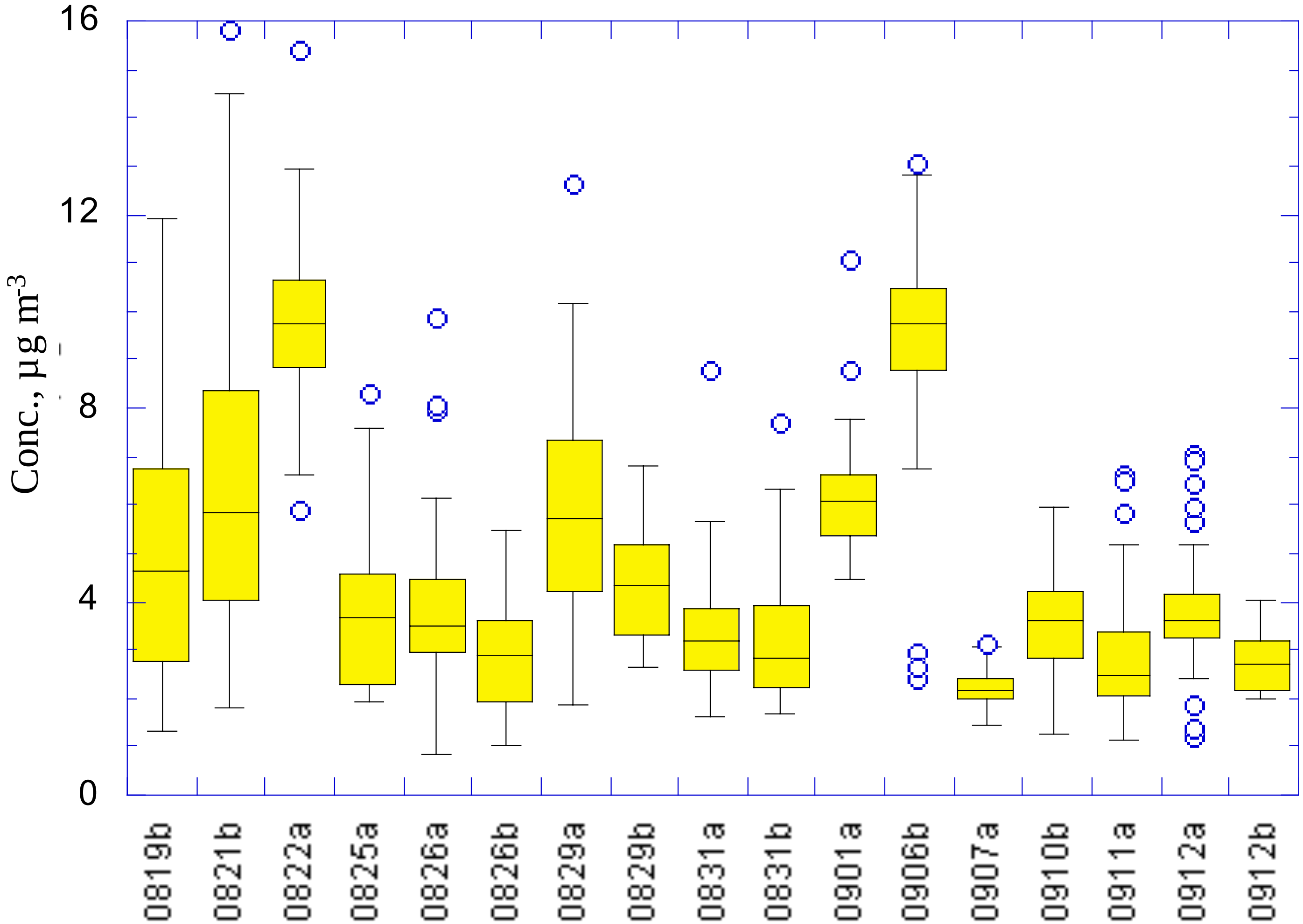


The PILS-IC Deployed on the DOE G1 during TexAqs 2000

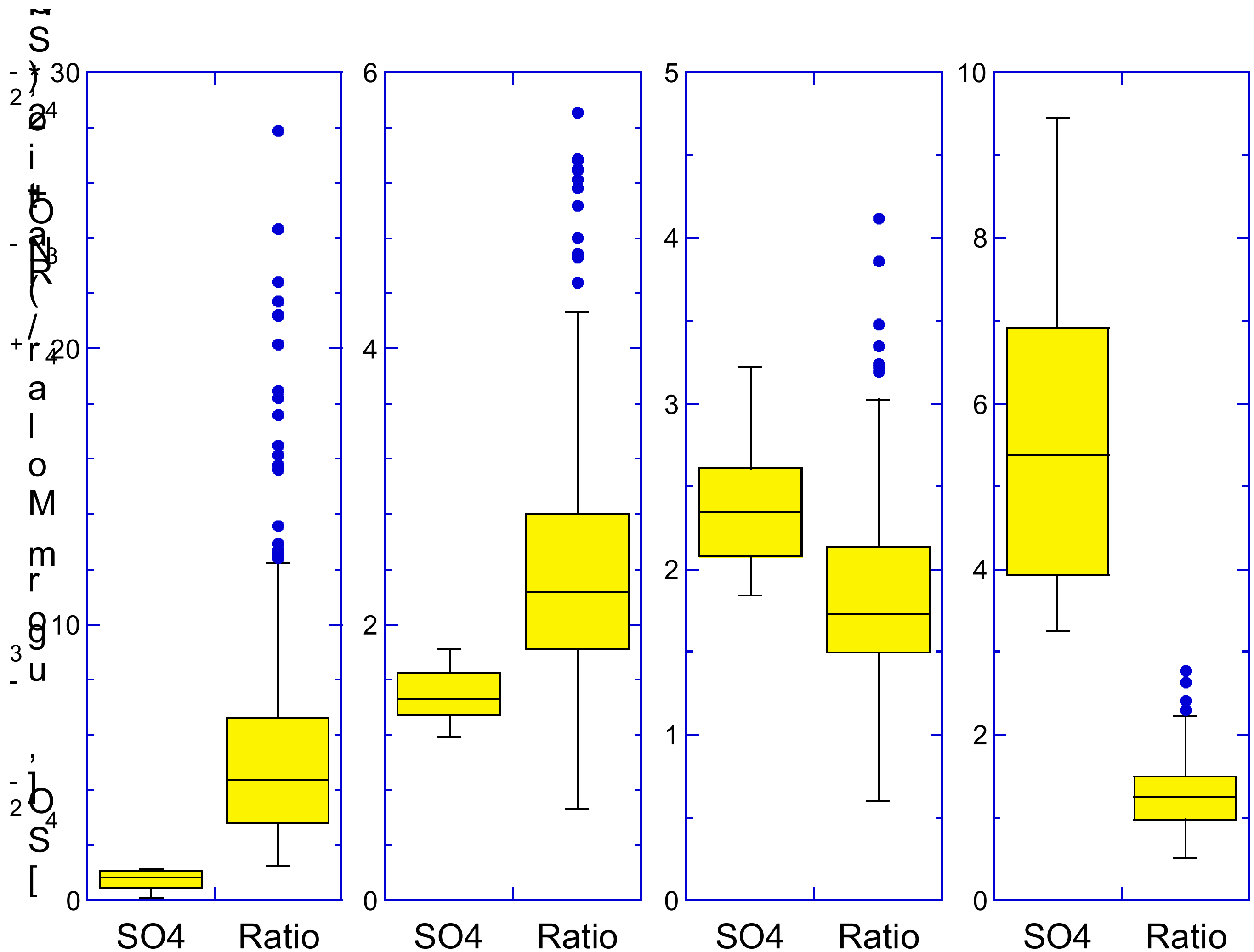
Frequency distributions of aerosol ionic concentrations
G1, TexAqs 2000



Distribution of aerosol ion mass concentrations
G1, TexAqs 2000



Ratios of $[NH_4]$ to $2x[SO_4]+[NO_3]$ as a function of SO_4 mass concentration in 4 quartiles



Other aerosol measurements on board the G1

Passive Cavity Aerosol Spectrometer Probe (pcasp)	*Number distribution in 15 bins between 0.1 µm and 3.0 µm*
Particle Soot Absorption Photometer (PSAP)	*Absorption coefficient at 565 nm due to black carbon*
Forward Scattering Spectrometer Probe (FSSP)	Number distribution in 15 bins between 2 µm and 47 µm
Twin Scanning Electrical Mobility Sizer (TSEMS)	Number distribution in the range from 3 nm to 700 nm

Additional characterization of aerosols

Pcasp data	§ Integrated particle surface and *volume* concentrations § Estimate of *total mass* of the accumulation mode particles with assumed densities (e.g., 1.7 g cm^{-3} for $(HN_4)_2SO_4$, and 1 g cm^{-3} for organics)
PSAP data	§ Estimate of *black carbon mass* concentration with an assumed σ value of 10 m^2 g^{-1}.
Surrogate organic mass	§ Tentative '*organic mass*' (an upper limit) = total mass – total ion mass – black carbon

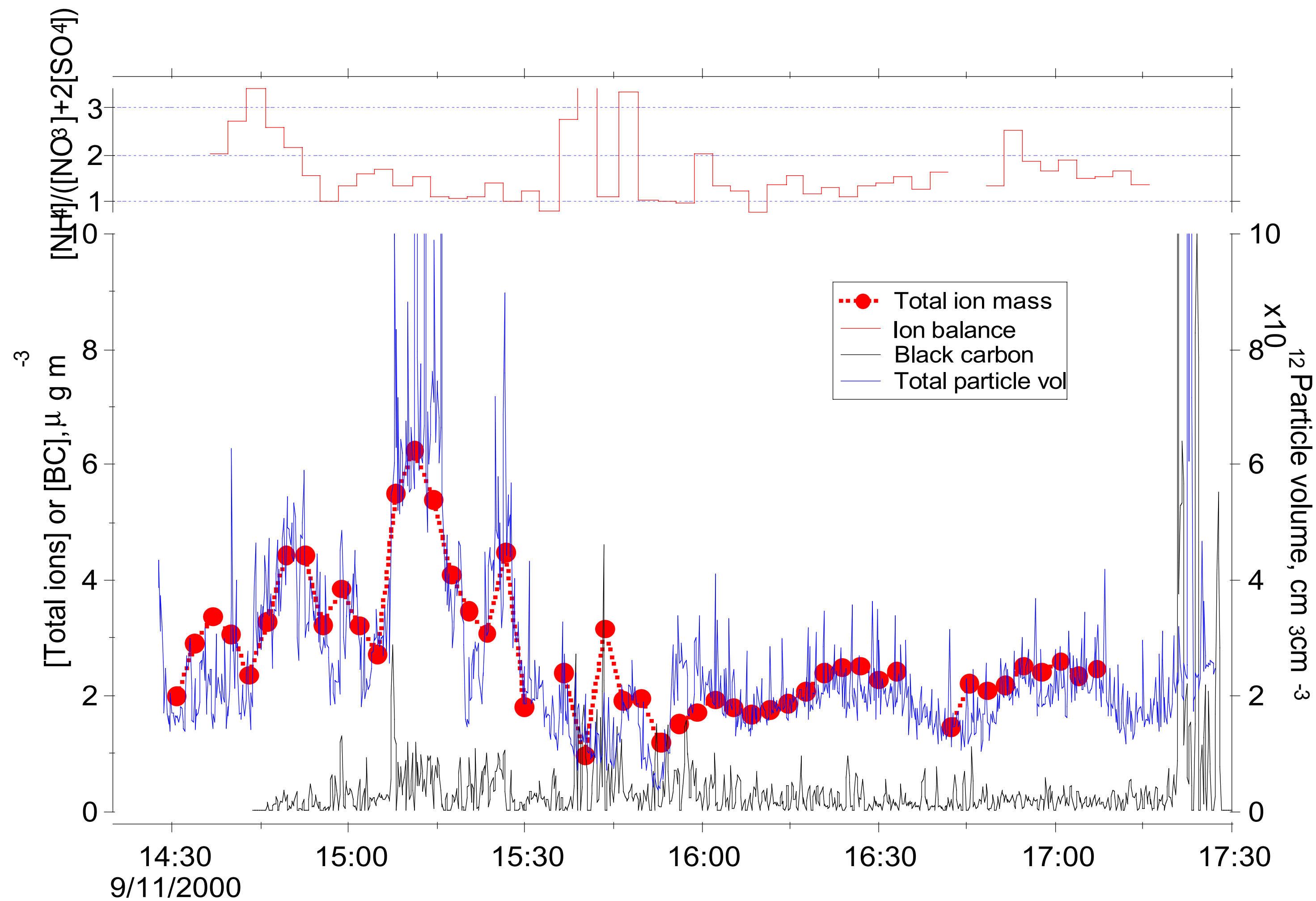
Aerosol Organic Component Determination

- Typically by filter collection followed by EC/OC determination based on the thermal optical reflectance technique
  - *Low time resolution (1 hr or longer)*
  - *Positive interference by gaseous organic compounds*
  - *Negative interference due to evaporative loss on filter medium*
  - *EC/OC subject to operational definition arising from, e.g., charring of OC*
  - *Uncertainty in the conversion factor from carbon to compound*
- Large measurement uncertainties associated with the OC determination

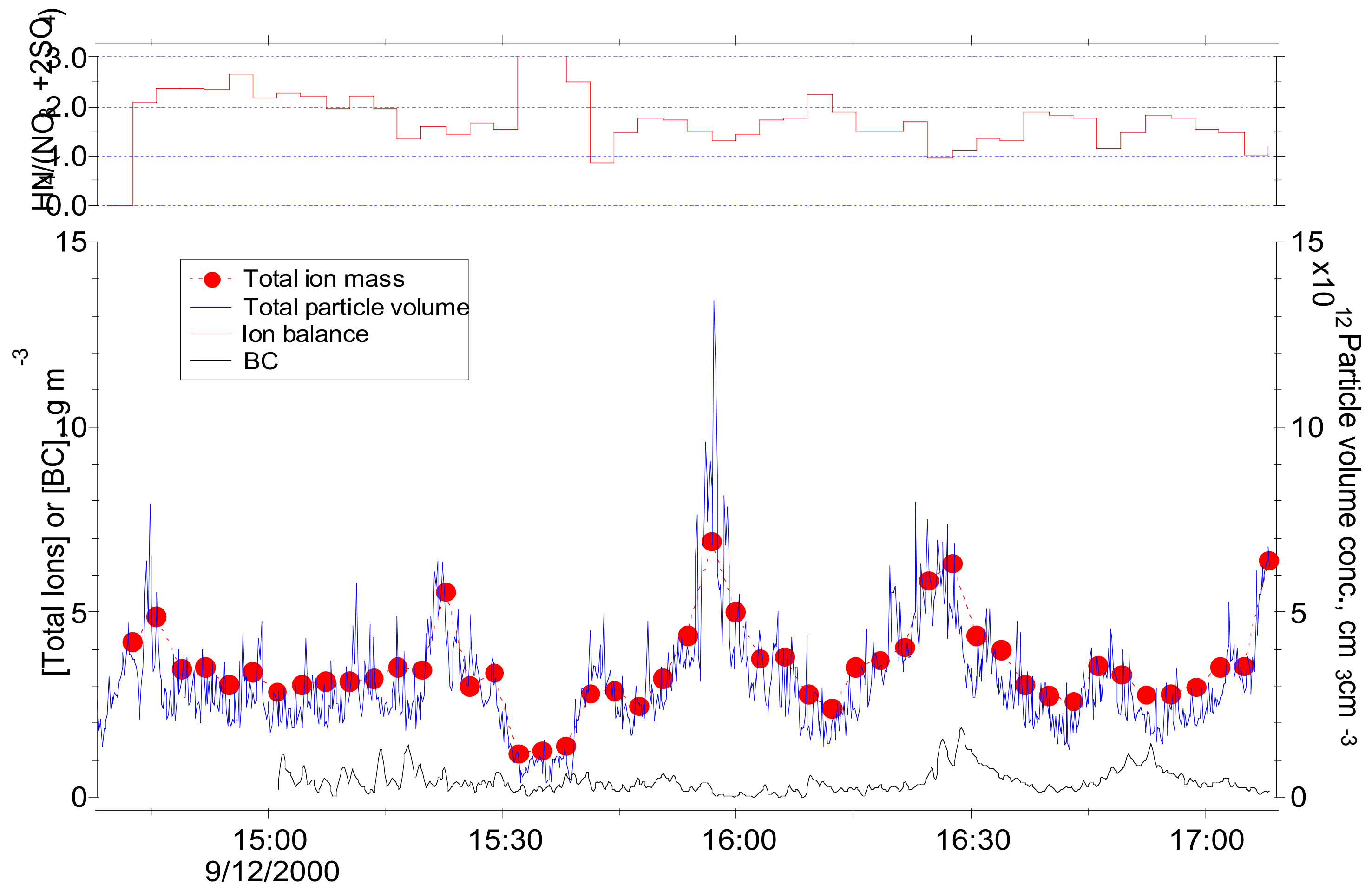
Questions on aerosol mass, chemical composition, and formation mechanisms

- *How much does the inorganic ion mass account for total aerosol mass?*
- *How much the black carbon and organic compounds contribute to total aerosol mass?*
- *What relationships can be discerned among these components, and what are their sources?*
- *Is there a size dependence of these components?*
- *Are there photochemical signals in these components?*

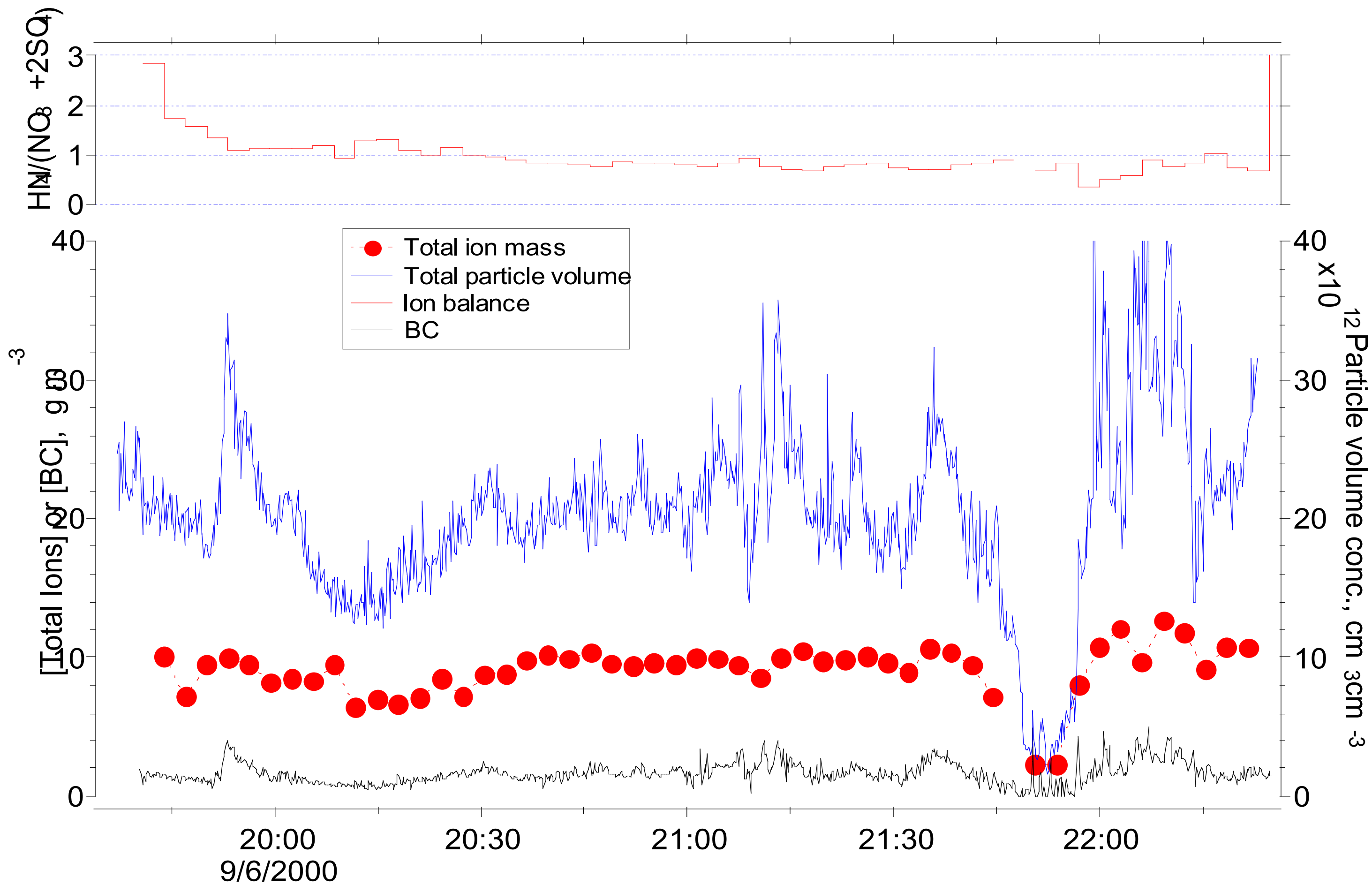
Comparison of total aerosol ion mass and particle volume 9/11/00



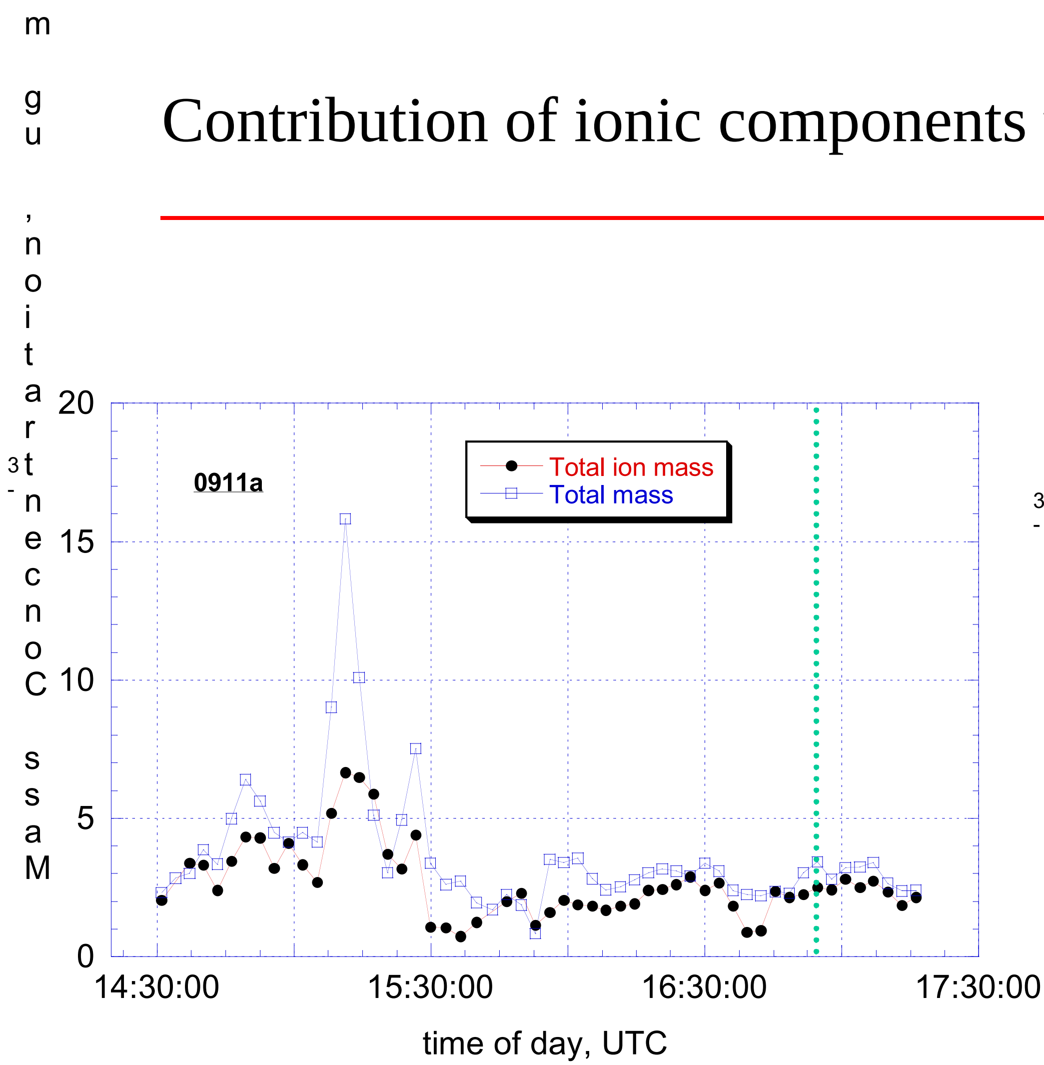
Comparison of total aerosol ion mass and particle volume 9/12/00

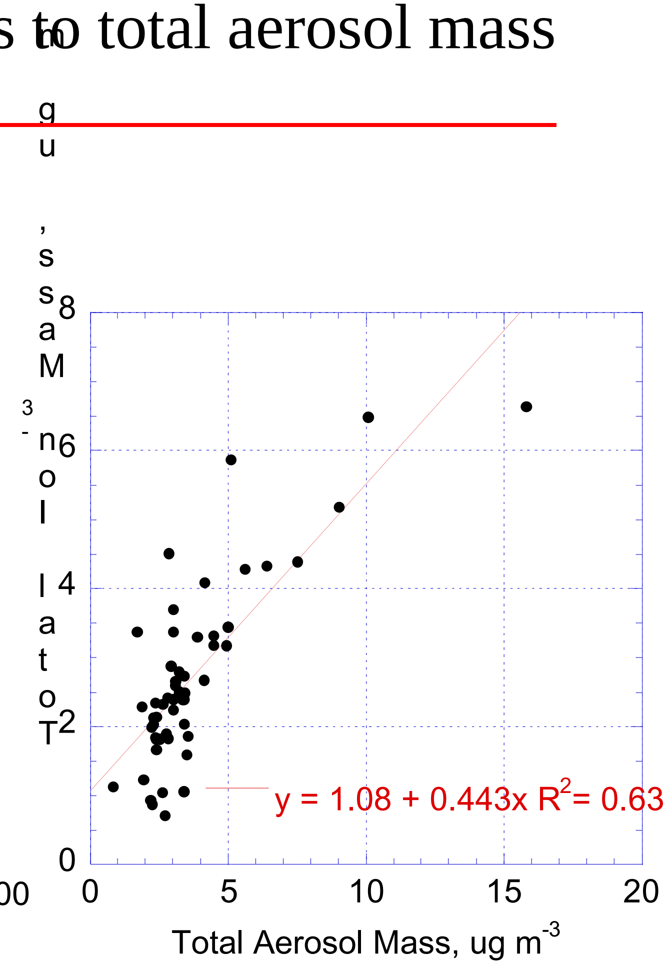


Comparison of total ion concentration and total particle volume 9/6/00

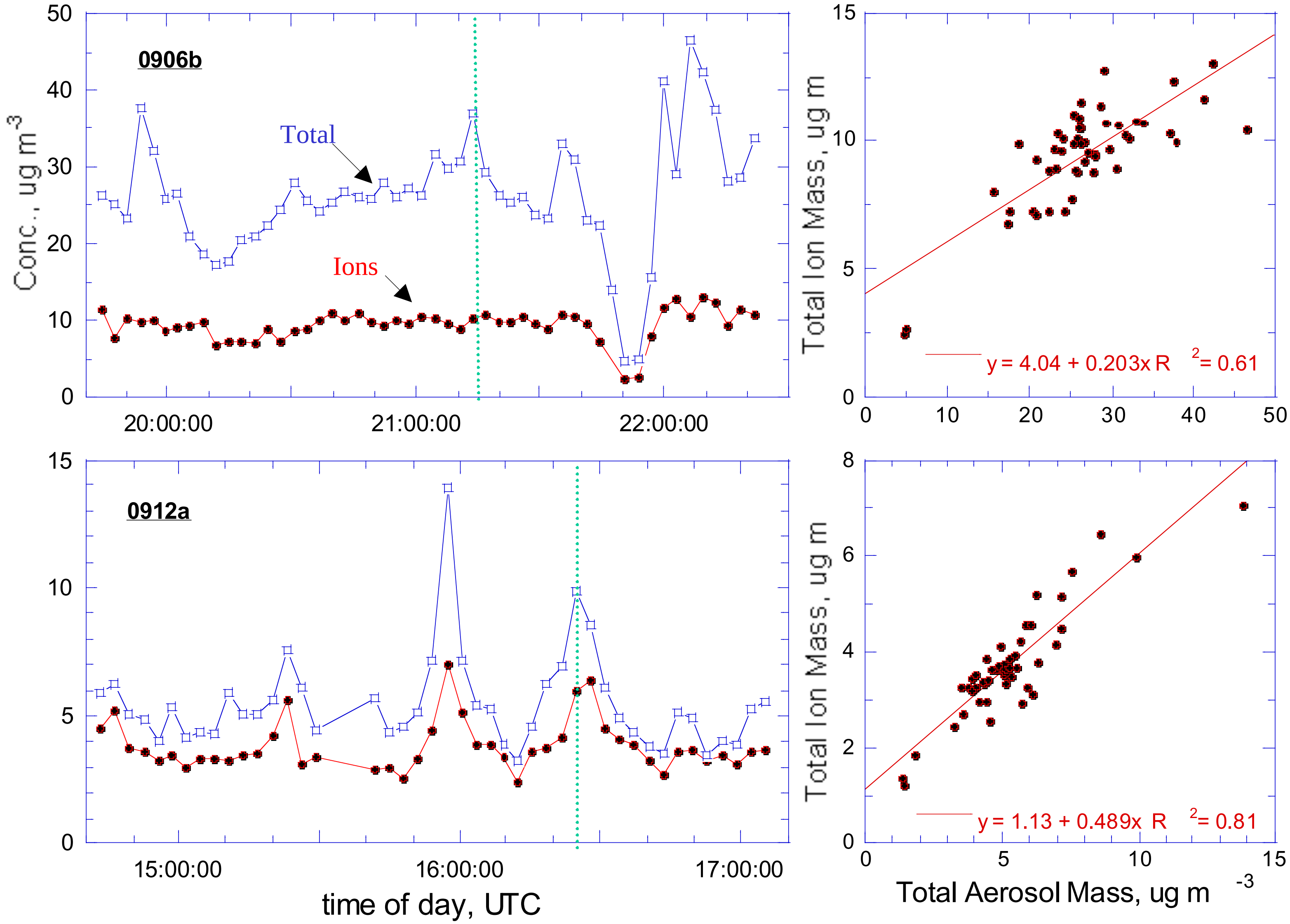


Contribution of ionic components to total aerosol mass

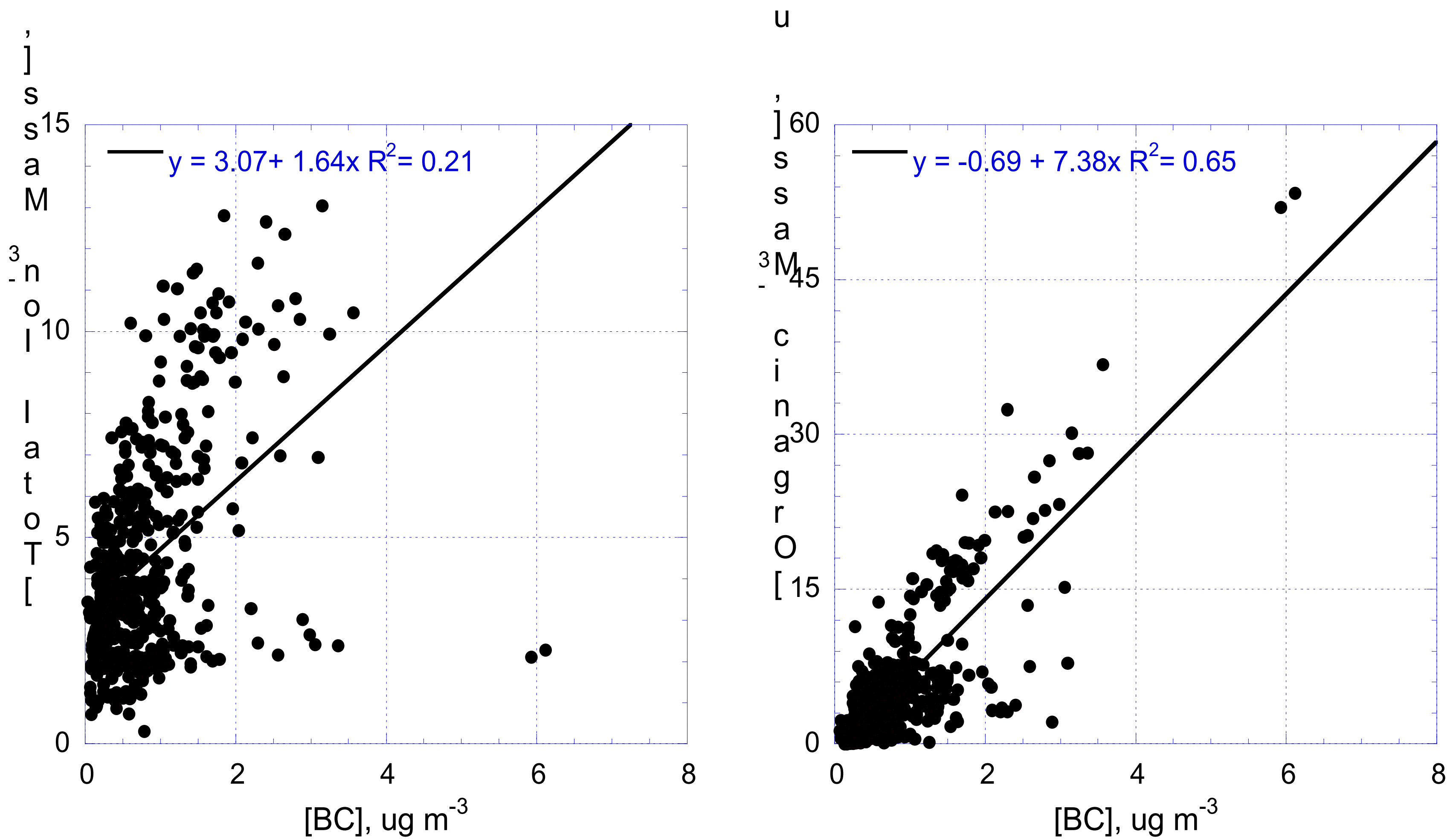




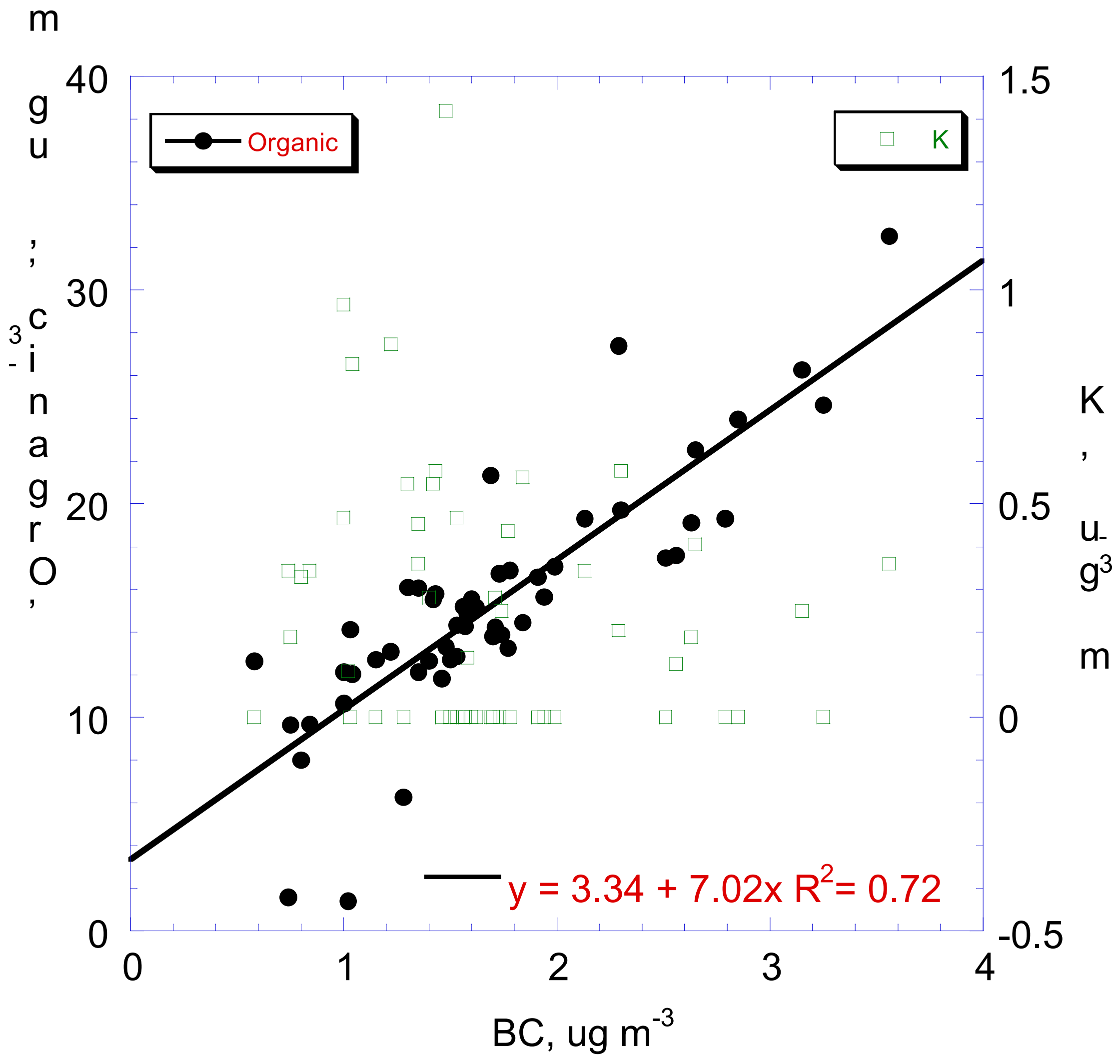
Contribution of ionic components to total aerosol mass

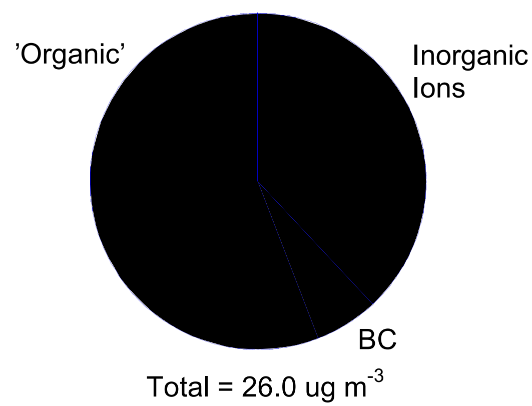


Relationships Among Aerosol Components



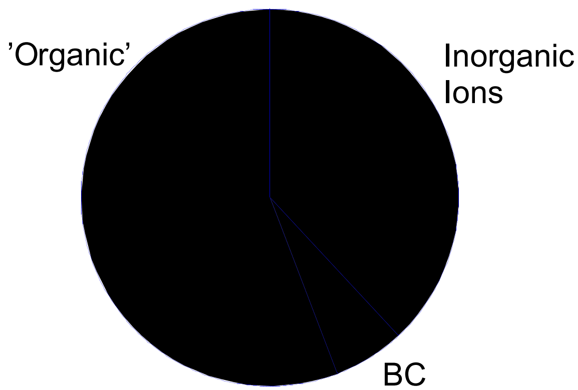
Aerosol Chemical Composition Observed on 9/6/00





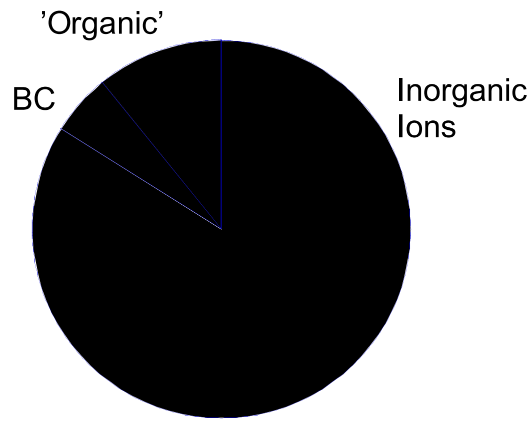
Comparison of aerosol chemical composition

9/6/00



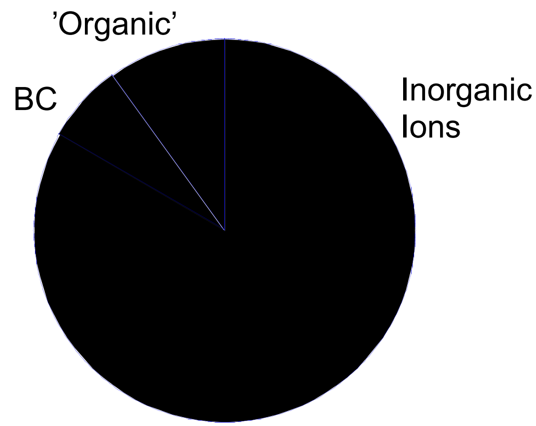
Total = 26.0 ug m^{-3}

9/11/00



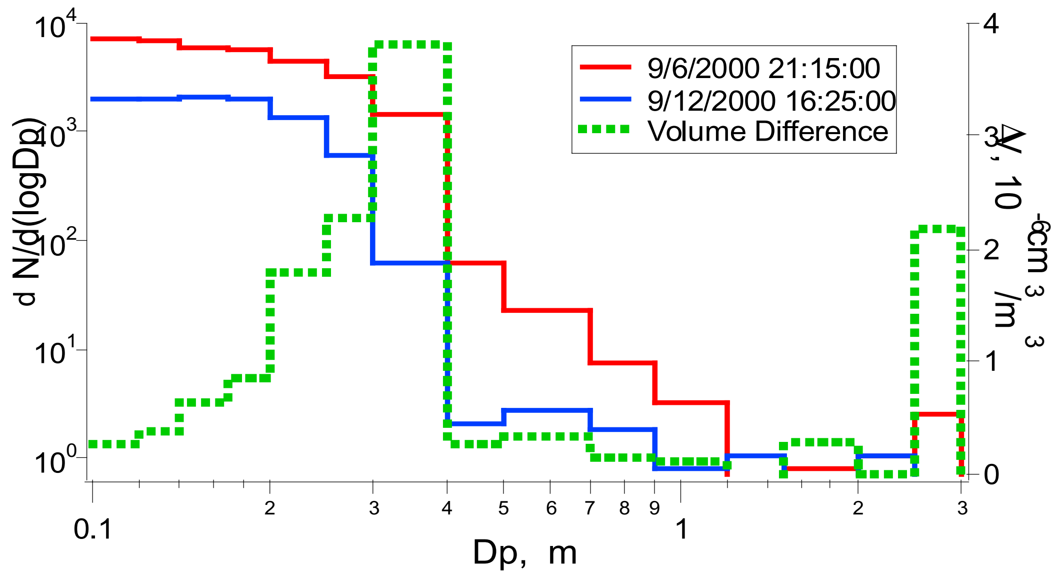
Total = 2.80 ug m^{-3}

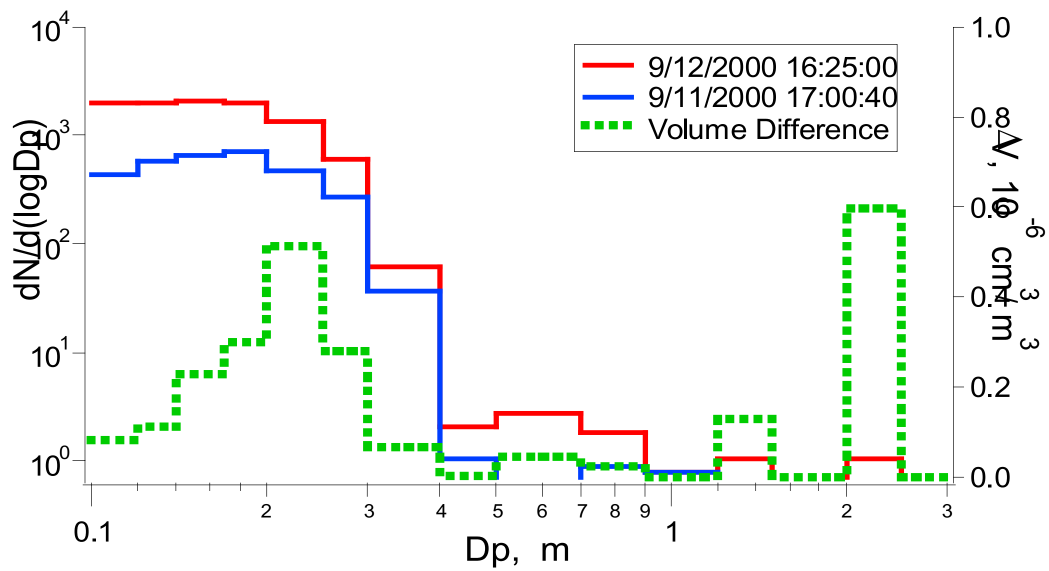
9/12/00



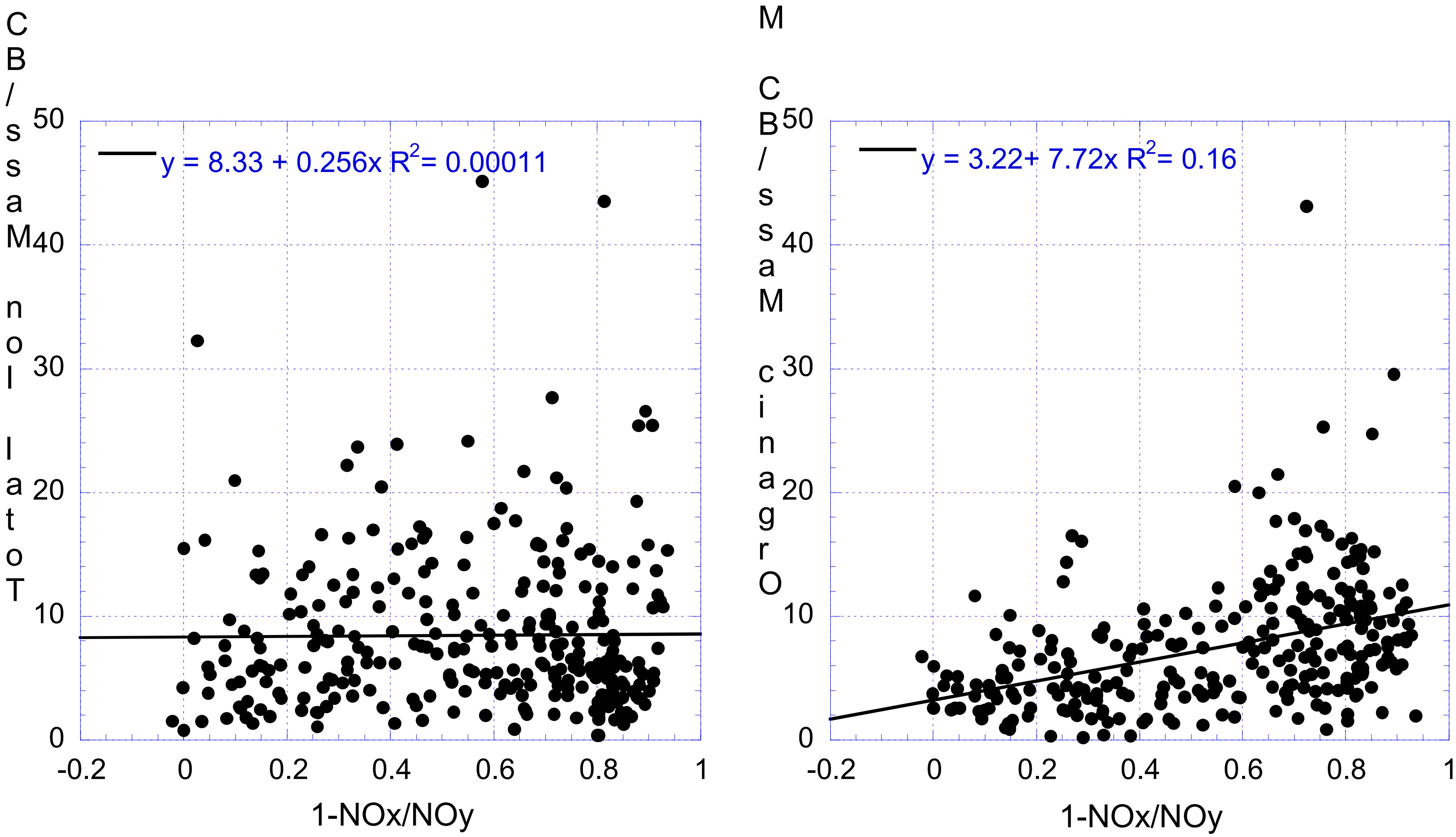
Total = 4.35 ug m^{-3}

Size Dependence of Aerosol Chemical Composition

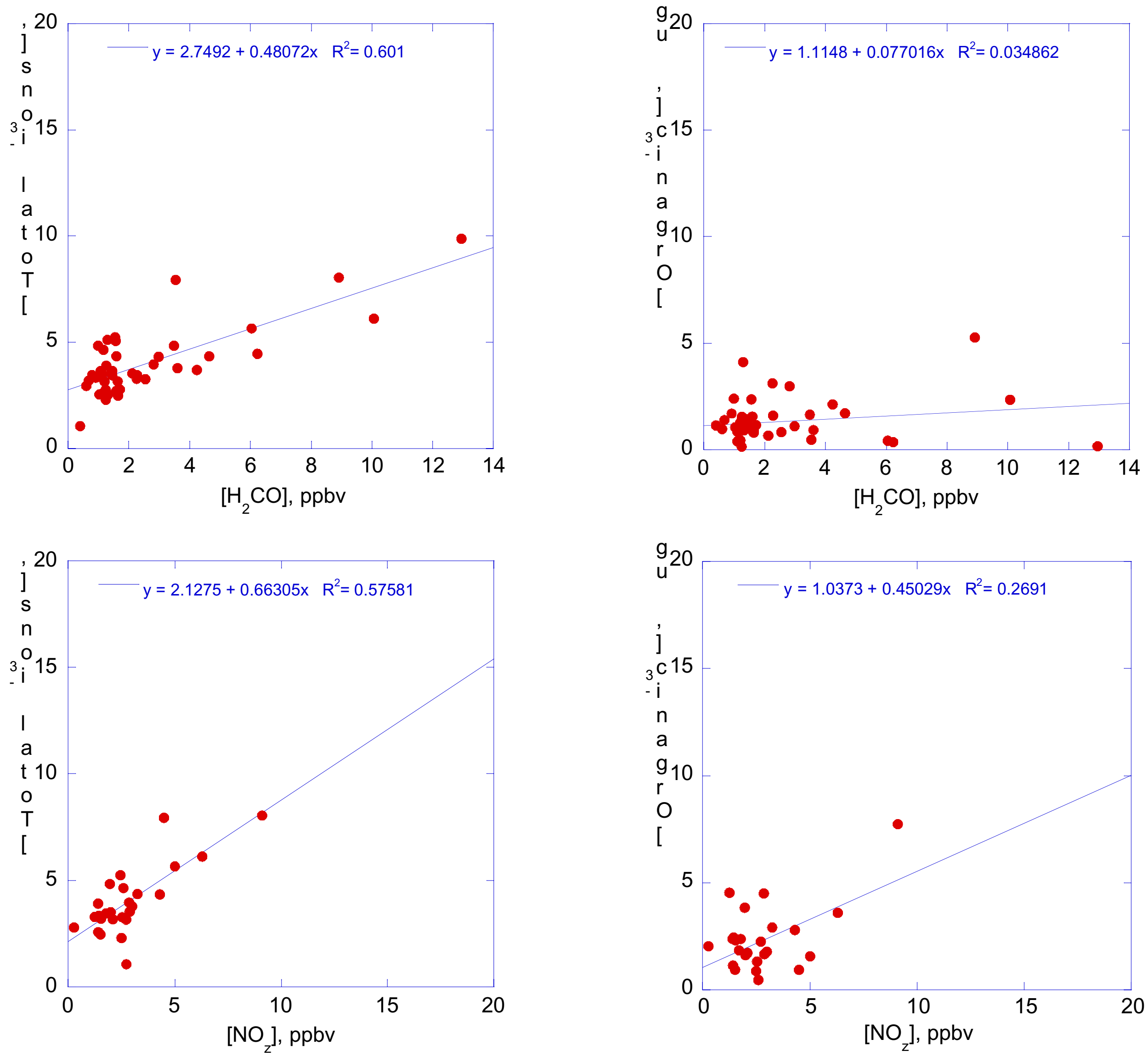




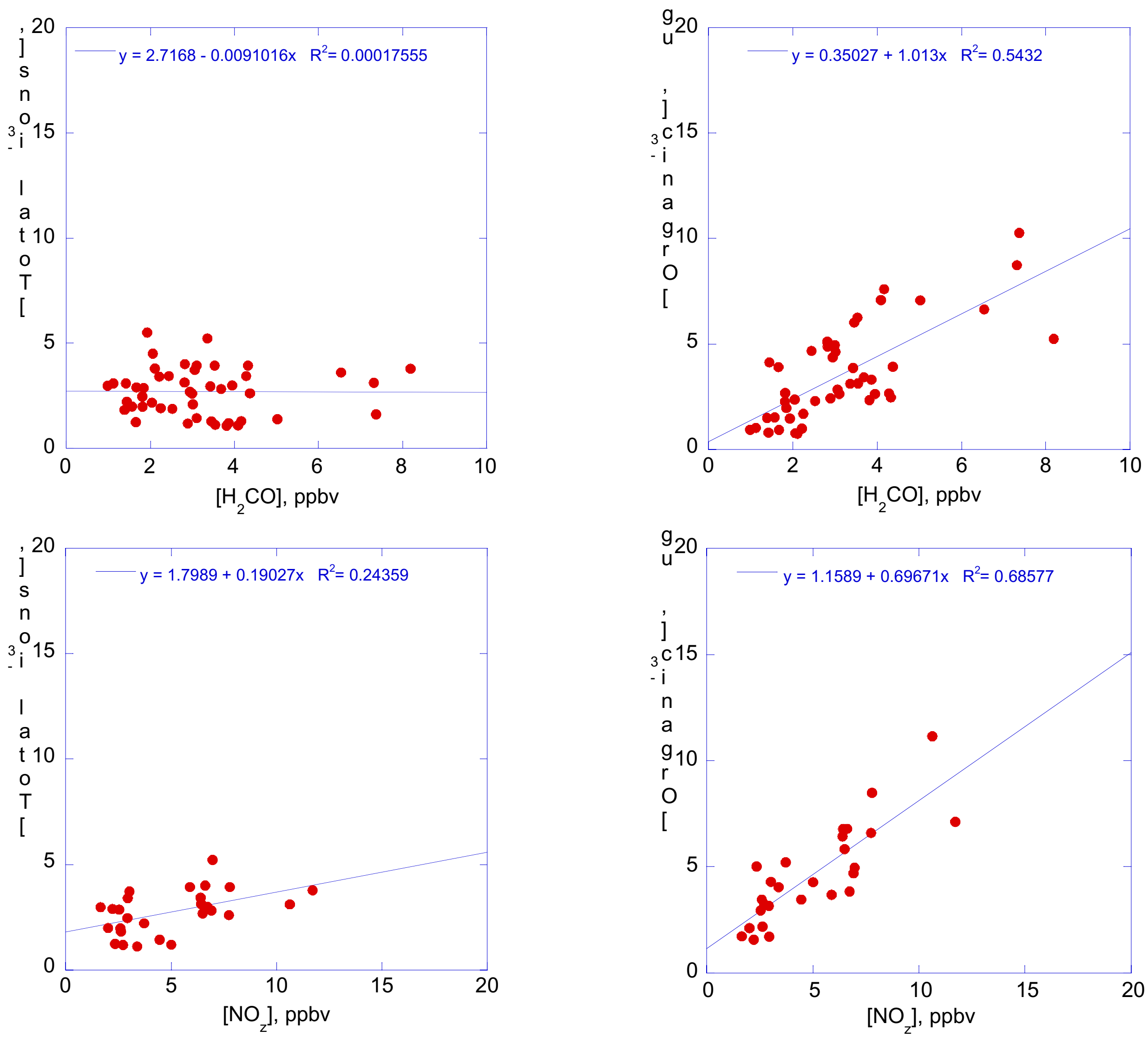
Aerosol mass loading as a function of photochemical age



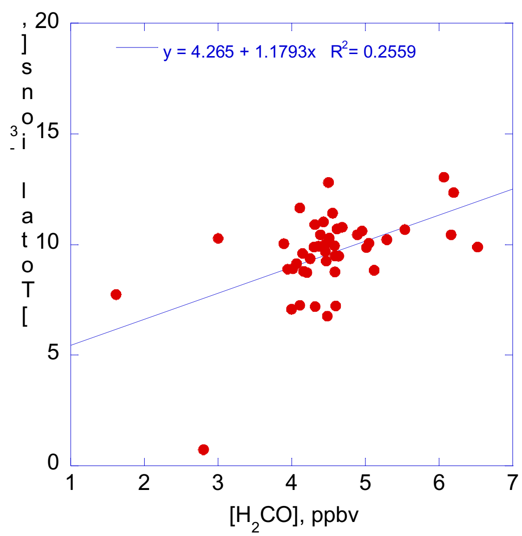
Relationships between aerosol mass and photochemical products morning flight, 8/26/00

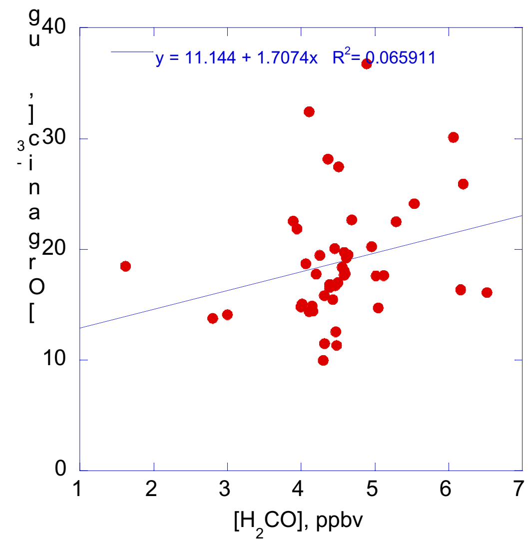


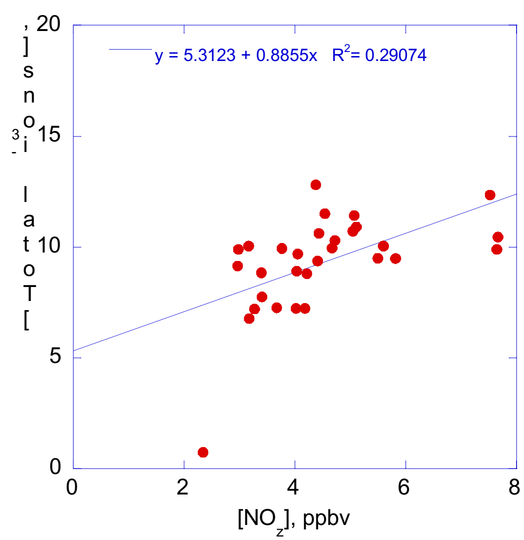
Relationships between aerosol mass and photochemical products afternoon flight, 8/26/00

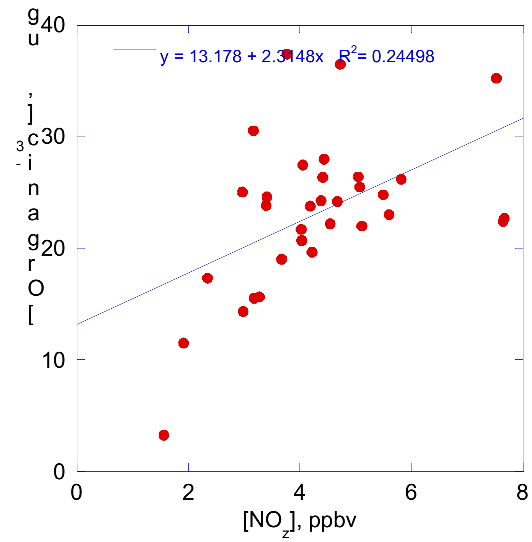


Relationships between aerosol mass and photochemical products afternoon flight, 9/6/00

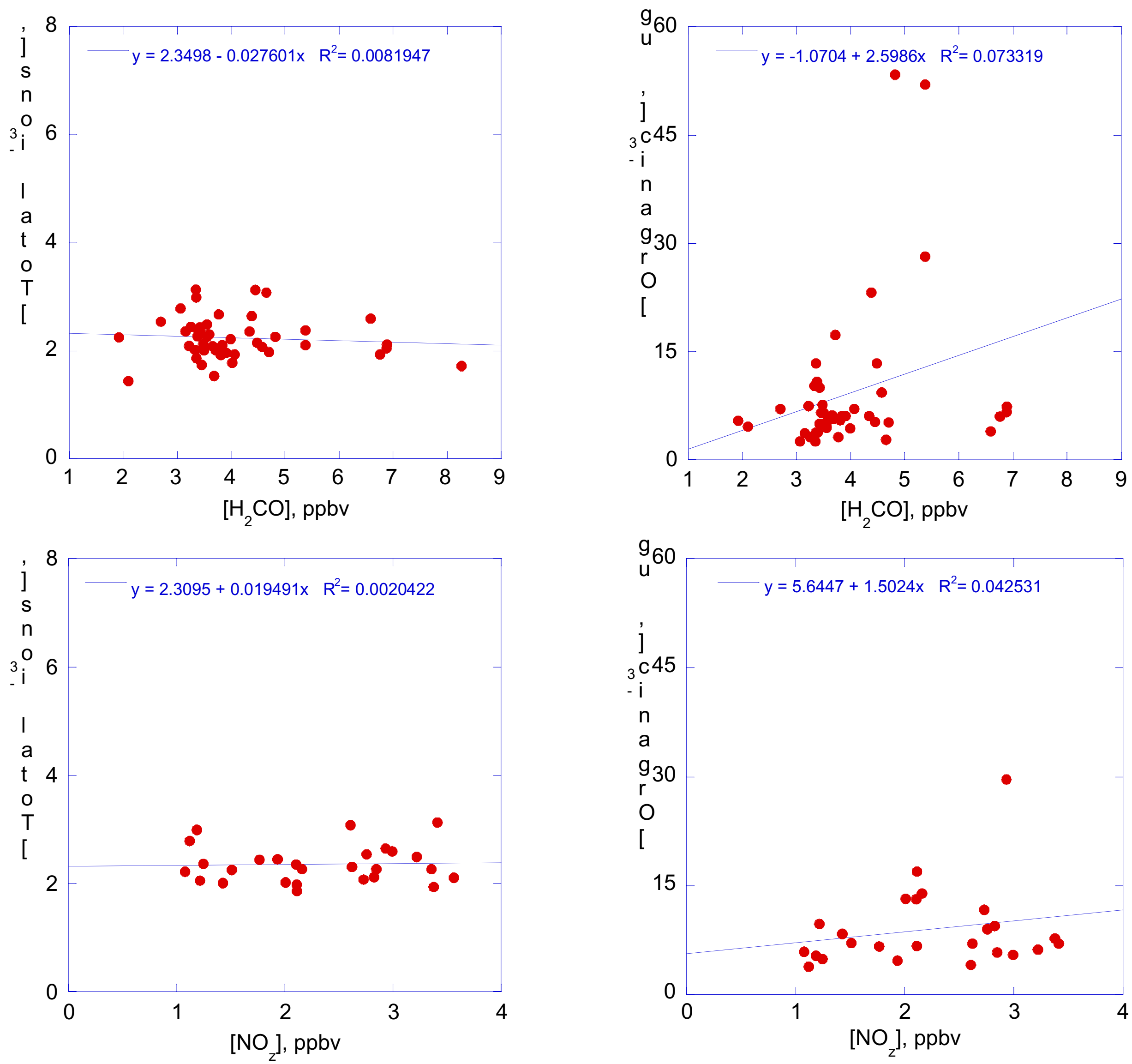




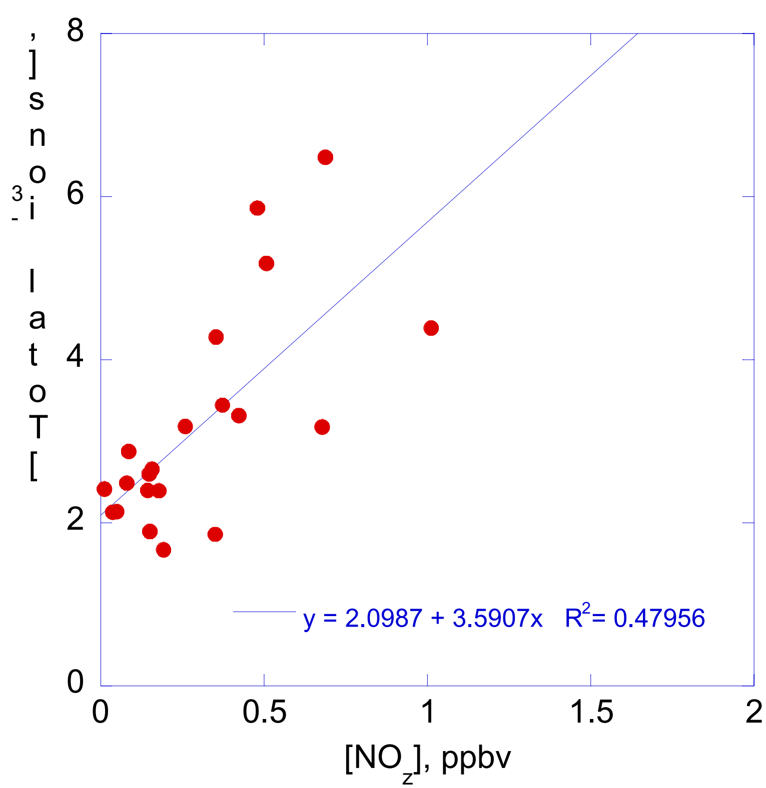


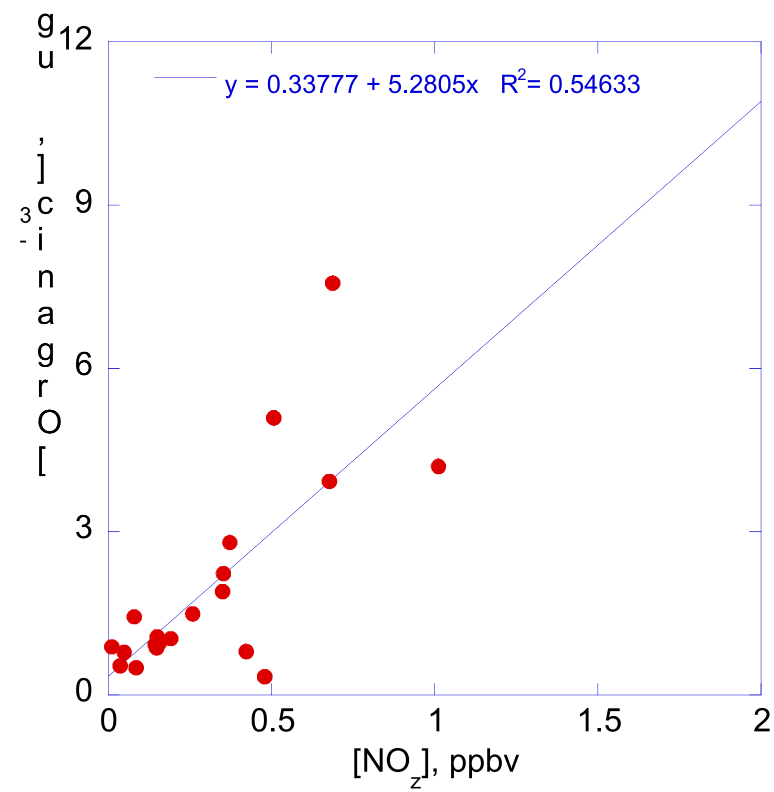


Relationships between aerosol mass and photochemical products
morning flight, 9/7/00



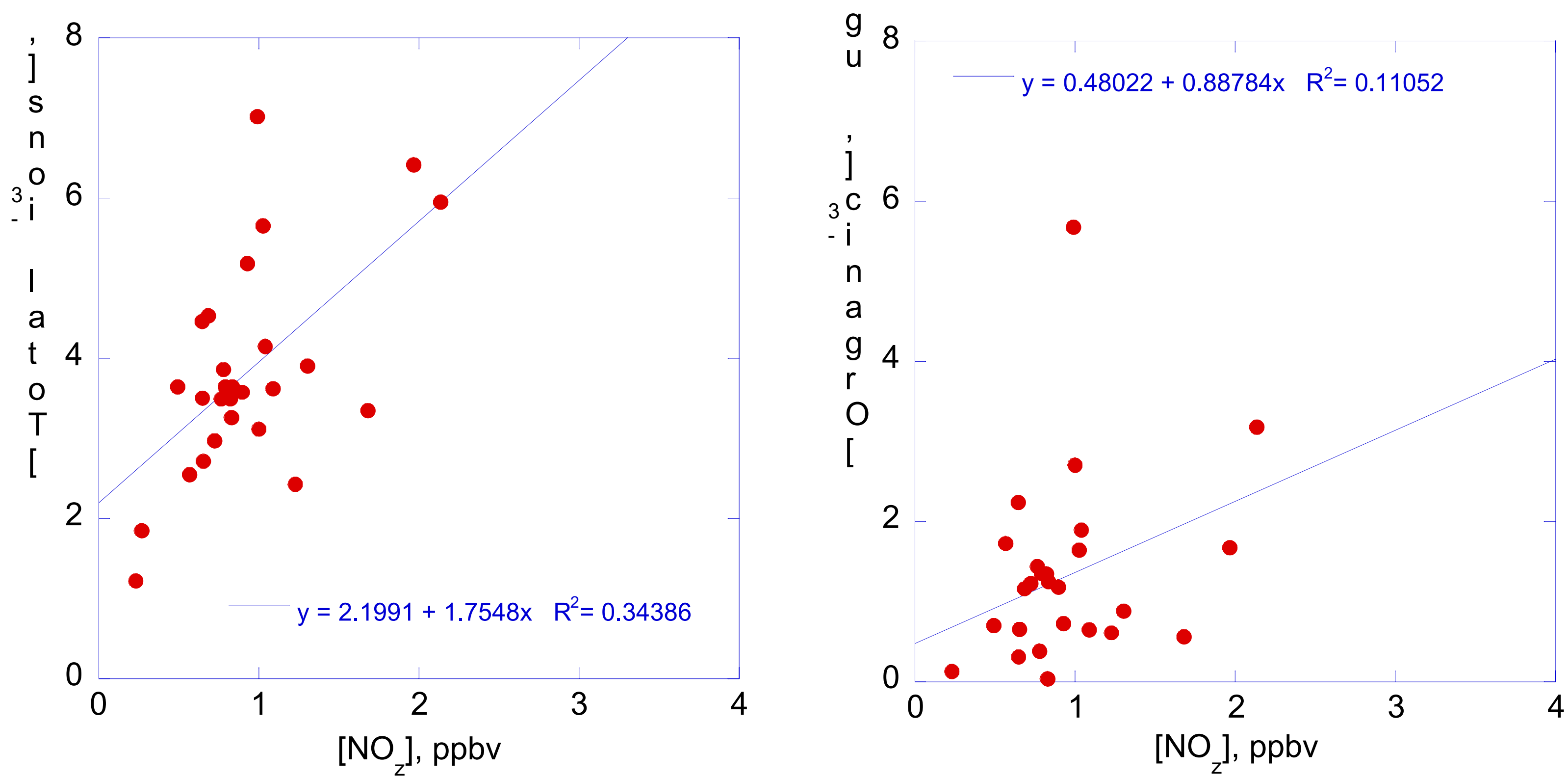
Dependence of aerosol mass on NO_z
morning flight, 9/11/00





Dependence of aerosol mass on NO_z

morning flight, 9/12/00



Conclusions

¥ Inorganic ions, black carbon, and surrogate organics of fine aerosol particles were determined on board the DOE G1during TexAqs 2000.

¥ NH_4^+ and SO_4^{2-} were the dominant ionic species; NO_3^- was typically small, < 0.5 mg m^{-3}, with infrequent excursions reaching half as SO_4^{2-}.

¥ The $[NH_4^+]$ to $[NO_3^-]+2[SO_4^{2-}]$ molar ratio often exceeded unity, suggesting the presence of other ionic species such as organic acids, and that NH_3 was in abundant supply.

¥ An organic aerosol event showed a mass maximum at ~0.4 m, contrasting that at ~0.2 m observed during a sulfate aerosol event.

¥ The aerosol organic component correlated well with black carbon, and contributed nearly equally to aerosol mass as the inorganic ions.

¥ Fine aerosol mass, both the inorganic and organic fractions, showed a positive correlation with H_2CO and NO_z, suggesting a photochemical source of aerosol precursors.